

NOTES ON PARTITIONING-RELATED TOPICS IN SUPPORT OF DISCUSSIONS WITH USEPA ON DRAFT LPR RI COMMENTS

During the June 28, 2016 modeling meeting, CPG proposed a simplified partitioning framework (termed “SHREQ”) for the CFT model that takes account of desorption kinetics. USEPA Region 2 voiced no initial objections to this framework and requested the following:

1. Further details on the derivation of Equation 16 in the partitioning framework notes provided to Region 2 on June 27, 2016.
2. Literature values of the “fraction equilibrium” parameter (f_E)
3. Refinement of parameterization of the partitioning framework:
 - Refine the f_E and f_d values used in partitioning notes.
 - Further characterize the algal carbon to total POC ratio to account for potential spatial variability, drawing on monitoring data from the New Jersey Harbor Dischargers Group (NJHDG) if possible.

Further Details on the Derivation of Equation 16 in the Partitioning Notes Provided to Region 2

The relevant text from the notes provided on June 27, 2016 is shown below:

$$f_d = \left(\frac{(1 + a \cdot K_{ow} \cdot [\text{DOC}])}{1 + f_E K_{oc} \cdot [\text{detrital POC}] + a \cdot K_{ow} \cdot [\text{DOC}] + a_{phy} \cdot K_{oc} \cdot [\text{Algal POC}]} \right) f_E \quad (13)$$

Equation 13 was solved for f_E as a function of the observed operationally dissolved fraction f_d from the hv-CWCM measurements:

$$f_E = \frac{f_d (1 + a \cdot K_{ow} \cdot [\text{DOC}] + a_{phy} \cdot K_{oc} \cdot [\text{Algal POC}])}{1 + a \cdot K_{ow} \cdot [\text{DOC}] - K_{oc} \cdot [\text{detrital POC}] \cdot f_d} \quad (16)$$

The steps in deriving Equation 16 from Equation 13 are provided below:

Derivation

Set:

$$\begin{aligned} \phi &\equiv \frac{[DOC]}{[DOC] + [P]} \\ \phi &\equiv \frac{[DOC]}{[DOC] + [P] + [D] + [A]} \\ \phi &\equiv \frac{[DOC]}{[DOC] + [P] + [D] + [A]} \end{aligned}$$

Which simplifies Equation 13 to:

$$\phi = \frac{(1 + \phi) \phi}{1 + \phi + D + A}$$

Solving for ϕ :

$$\phi(1 + \phi + D + A) = (1 + \phi)\phi \quad (\text{Step-A})$$

$$\phi(1 + D + A) + \phi^2 = (1 + \phi)\phi \quad (\text{Step-B})$$

$$\phi(1 + D + A) = (1 + \phi)\phi - \phi^2 \quad (\text{Step-C})$$

$$\phi(1 + D + A) = (1 + \phi - \phi)\phi \quad (\text{Step-D})$$

$$\phi = \frac{(1 + D + A)}{(1 + \phi - \phi)} \quad (\text{Step-E})$$

Substituting terms back in yields Equation 16 in its final form from the notes:

$$\phi = \frac{1 + [DOC] + [P] + [D] + [A]}{1 + [DOC] + [P] + [D] + [A]}$$

Literature Values of the “Fraction Equilibrium” Parameter

The proposed partitioning framework expresses the influence of sorption kinetics in a simplified manner via a parameter termed the “fraction equilibrium” (ϕ), which represents the fraction of contaminant mass that would be modeled as undergoing instantaneous equilibrium partitioning in the water column. Conceptually, the fraction equilibrium value in a full kinetic desorption model represents sorption sites (e.g., carbon) that are accessible for rapid contaminant exchange with the surrounding water, while the remainder of the sorption sites are shielded and less accessible via rate limited diffusion (Haggerty and

Gorelick 1995). The K_{oc} value is in this context dependent on the nature of the solids. Within the proposed simplified framework, K_{oc} is subject to additional site-specific and contaminant-specific effects such as flow and solids dynamics, boundary conditions, and sediment initial conditions. It is therefore preferred to use site-specific data to parameterize K_{oc} within the proposed partitioning framework. The notes provided to Region 2 demonstrated one approach to using the hv-CWCM data to estimate K_{oc} in a manner consistent with this framework.

To help guide and interpret K_{oc} values derived from the hv-CWCM data and in response to Region 2's request, values inferred from desorption experiments reported in the literature are provided below. The values are summarized in an approximate manner and no attempt has been made to reconcile potential site- and experiment-specific influences (e.g., the nature of the solids, the time history of contamination, the definition of the reported desorption phases, and the length of the experiments). These values demonstrate that kinetic desorption effects have been observed for many hydrophobic contaminants and sites, and that the range of K_{oc} values is fairly large.

- The compilation by Pignatello and Xing (1996; included herein as Figure 1) suggests K_{oc} values of 0.55 to 0.83 for PCBs in river sediments (based on [1 – the reported “slow” fraction]). It also suggests K_{oc} values ranging from 0.04 to 0.9 for a variety of other contaminants and experimental setups.
- Sormunen et al. (2009) experimental data suggest K_{oc} values of approximately 0.3 for 2,3,7,8-TCDD, based on four different test sediments from three water bodies.
- Carroll et al. (1994) experimental data on Hudson River sediments suggest K_{oc} values of approximately 0.4 to 0.6 for PCBs.
- Cornelissen et al. (2000) results imply K_{oc} values of approximately 0.19 for ten PAHs, 0.14 for four PCB congeners, and 0.04 for nine chlorobenzenes based on six different sediments, which are similar to the findings of Hulscher et al. (1999) for the same compound classes (an K_{oc} value of about 0.2 is inferred).
- Chai et al. (2006) measurements imply K_{oc} values ranging from approximately 0.2 to 0.5 for four different PAHs based on two different sediments.

Refinement of Parameterization of Partitioning Framework

It is anticipated that the analysis of K_{oc} using the hv-CWCM data will be refined following feedback from Region 2 on the proposed framework and its parameterization (e.g., the requested use of a spatially variable algal carbon ratio). Several discussion points are proposed below to ensure the assumptions and methodology applied are consistent between the hv-CWCM analysis used to parameterize the partitioning framework and the RCATOX code, so that Region 2 and the CPG can agree on the best path forward in refining the analysis.

As outlined in the partitioning notes provided on June 27, 2016, the hv-CWCM data may be used to derive site-specific K_{oc} values. The hv-CWCM data used for this purpose are:

- Fraction dissolved
- Total POC
- DOC

The key input parameters used to derive K_{oc} are:

1. Equilibrium partitioning coefficients K_{ow} and K_{ow}^*
2. Binding affinity constants for algae and DOC: $K_{d,alg}$ and $K_{d,DOC}$
3. Temperature and Salinity adjustment parameters: ΔH_{ow} and ΔS_{ow}
4. Algal carbon fraction: the algal carbon to total POC ratio

Parameterization topics to discuss at the September 20 modeling meeting include:

1. Equilibrium partitioning coefficients: K_{ow} and K_{ow}^*
 - Apparent K_{ow} values derived from water column data cannot be interpreted as equilibrium values because they are subject to kinetic impacts.
 - Use of literature K_{ow} values
 - Use of literature K_{ow} values supplemented by K_{ow}^* values and K_{ow}^*/K_{ow} relationships. For example:
 - $\log K_{ow}^* = 0.72 \cdot \log K_{ow} + 0.49$ (Schwarzenbach and Westall 1981)
 - $K_{ow}^* = 0.411 \cdot K_{ow}$ (Karickhoff 1981)
 - Treatment of the modeled carbon forms in RCATOX
 - Detrital and algae sorption are $K_{d,det}$ and $K_{d,alg}$
 - DOC sorption is $K_{d,DOC}$

- The difference can be important when □ and □ differ significantly
 - One option is to rewrite □ as a function of □ (see sample relationships above)
 - If not using apparent □ values, the difference between literature □ and □ may be small and this distinction may not matter much
2. Binding affinity constants for algae and DOC - □ and □
- Should be made consistent with choice of □ and □ values above
3. Temperature and Salinity adjustments – Δ □ and □
- Should be included in the SHREQ □ analysis if used in RCATOX code, for consistency
 - Currently □ is adjusted for temperature and salinity, but □ may not be
 - i. The CARP report (HQI 2007) notes adjustments for □ but it is unclear whether the code implementation matches, as described in the notes below; issue to be resolved at the modeling meeting.

The RCATOX code calculates the variable KOCV, which corresponds to the KOC adjusted by temperature and/or salinity. KOCV is used for sorption to particulate and algal carbon in the code snippet below (from `toxics_as.f`).

```

DO 40 IOC=1,NPC
  IF (IOC.LT.3) THEN
    PART (NOSS+IOC) = A00C (ICH,IOC) * KOCV
                    / ( 1 + KPHYUPTK (ICH) * A00C (ICH,IOC) * KOCV )
  ELSE
    PART (NOSS+IOC) = A00C (ICH,IOC) * KOCV
  ENDIF

```

However, it appears that the unadjusted KOC is used for DOC sorption rather than KOCV; see code snippet below (note that in the EPA model inputs for 2,3,7,8-TCDD, $KOC * A_{OOC}$ is equivalent to $0.08 * \square\square\square\square\square\square$)

```
      SORBED TO ORGANIC CARBON
      DO IOC=1,NPC
        DISFCT (NOSS+IOC) =PART (NOSS+IOC) *ORGCRB (IOC) *1.E-06
      ENDDO
      SORBED TO DOC
      DO I=1,NDC
        IF (ISEDFLAG.EQ.0) THEN
          DISFCT (NOSS+NPC+I) =KOC (ICH) *1.E-06*ORGCRB (NPC+I)
                                *A00C (ICH,NPC+I)
        ELSE
          DISFCT (NOSS+NPC+I) =KOC (ICH) *1.E-06*ORGCRB (NPC+I)
        ENDIF
      ENDDO
      IF (ISEDFLAG.NE.0) THEN
        DISFCT (NOSS+NPC+1) =DISFCT (NOSS+NPC+1) *CADOCS (ICH)
      ENDIF
```

4. Algal carbon fraction topics

- Status of data request submitted by CPG on August 12
- Options for characterizing a spatially variable fraction as proposed by Region 2 (e.g., using historical data and/or sv-CWCM data if NJHDG data are unavailable)

REFERENCES

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TABLE 1
Recent Examples of Observed Slow Sorption or Desorption in Natural Sorbents^a

	Uptake		approx ratio ^b $K_d^{app}(long)/K_d^{app}(short)$	slow fraction ^{a,c}	ref
	contact period (d)				
	long	short			
PCE in aquifer sand material	10	1	3	0.67	33
TeCB in aquifer sand material	100	1	10	0.90	33
pyrene in lake sediments	180	3	2	0.50	107
phenanthrene in lake sediments	180	3	2	0.50	107
picloram in various soils	300	7	1.5–3.9	0.33–0.74	126
lindane in subsurface fine sand	167	4.2	4	0.74	38
(corrected for abiotic hydrolysis)					
atrazine in soil	22	1		up to ~0.3	127
metolachlor in peat	30	1	1.4	0.22–0.33 ^d	55
metolachlor in soil	30	1	1.6	0.31–0.37 ^d	55
1,3-dichlorobenzene in peat	30	1	1.3	0.14–0.39 ^d	55
1,3-dichlorobenzene in soil	30	1	1.4	0.19–0.48 ^d	55
	Release		remaining slow fraction ^b	ref	
	sparging or leaching time				
PCB-contaminated river sediments	7-d continuous removal		0.17–0.45	28	
TCE-contaminated subsoil	seven 1-d washings or 24 000 column PV ^e		0.25–0.27	34	
TCE-, PCE-, toluene-, xylene-contaminated soils	14 washings over 7 d		0.48–0.94	128	
atrazine-contaminated soil	70-d leaching at 1 PV ^e /d		0.56	20	
metolachlor-contaminated soil	70-d leaching at 1 PV ^e /d		0.59	20	
naphthalene-contaminated soils	3-d gas purge		0.1–0.5	47	
EDB-contaminated soil	10-d batch desorption		0.96	25	
naphthalene-spiked soil (3–90 d contact)	3-d gas purge		0.1–0.2	47	
simazine-spiked soil	35-d in the field		0.9	27	
naphthalene-spiked soil (1-, 7-, 30-d contact)	many 2-h to 7-d washings		≥0.6	15	
phenanthrene-spiked soil (7–20-d contact)	10 washings over 178 d		0.62	15	
TCE-spiked soil (2.5-, 5.5-, 15.5-mo contact)	five 1-d washings		0.10, 0.25, 0.45	34	
PAHs on urban aerosols	28 d (130 m ³ of moist N ₂)		0.4–0.6	3	
atrazine on soil (4-, 12-, or 24-d contact)	six 6-d batch desorptions		0.35–0.55	127	

^a PCE, tetrachloroethene; TeCB, 1,2,4,5-tetrachlorobenzene; picloram, 4-amino-3,5,6-trichloropicolinic acid; lindane, γ -1,2,3,4,5,6-hexachlorocyclohexane; PCB, polychlorobiphenyl congeners; EDB, 1,2-dibromoethane; TCE, trichloroethene; atrazine, 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine; metolachlor, 2-chloro-*N*-[2-ethyl-6-methylphenyl]-*N*-[2-methoxyethyl]acetamide; simazine, 2-chloro-4,6-bis(ethylamino)-1,3,5-triazine.

^b Listed as estimates from graphs and tables in original work and may be rounded. ^c Slow fraction = $1 - K_d^{app}(short)/K_d^{app}(long)$. ^d Concentration dependent. ^e PV, column pore (void) volumes.

Figure 1

Table 1 from Pignatello and Xing (1996)

Source: Pignatello, J.J., and B. Xing, 1996. Mechanisms of slow sorption of organic chemicals to natural particles. *Environ. Sci. Technol.* 30:1-11

